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(54) **Insecticide formulations based
on pyrethroids and thiophosphoric
esters**

(57) **Stable, emulsifiable concentrates
exerting insecticide and acaricide
activity comprising:**

(A) 0.5 to 30% by weight of one or
more of: permethrine, cypermethrine,
deltamethrine, phenvalerate, α -cyano-
3-phenoxy-benzyl ester of 2,2-
dimethyl-3-(β -fluoro- or chloro- β -
trifluoromethyl-vinyl)cyclopropane
carboxylic acids,

(B) 0.5 to 50% by weight of one or
more of: dimethoate, prothoate,

phenthoate and pyridaphenthion,

(C) 0.3 to 2.5% by weight of 2-
hydroxy-4-octyloxy-benzophenone,

(D) 0.5 to 3% by weight of allyl-
glycidyl ether and/or phenyl-glycidyl
ether,

(E) 5 to 25% by weight of a
vegetable oil,

(F) 1 to 15% by weight of one or
more surfactants, and

(G) an amount sufficient to attain
100% by weight of composition, of
organic solvent selected from one or
more cyclohexanone and aromatic or
alkyl-aromatic hydrocarbons having
from 6 to 12 carbon atoms.

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SPECIFICATION

Insecticide formulations based on pyrethroids and thiophosphoric esters

This invention relates to formulations which are emulsifiable in water and are based on pyrethroids and thiophosphoric esters. In particular, the invention relates to insecticide and acaricide formulations based on pyrethroids and thiophosphoric esters which compositions do not undergo any significant alteration in the course of time due to temperature variations, and which are endowed with an improved stability in the field.

There are several known synthetic pyrethroids which exert an intense insecticide activity, examples of which include 3-phenoxy-benzyl or alpha-cyano-3-phenoxy-benzyl esters of 2,2-dimethyl-cyclopropanecarboxylic acids having a beta,beta-disubstituted vinyl group in the 3-position or of 2-(4-chlorophenyl)-3-methyl-butyric acid.

Another important class of insecticides are the phospho-organic derivatives (thiophosphoric and dithiophosphoric esters) which have been successfully employed for a considerable time.

However, both of the above classes possess disadvantageous properties, such as a restricted action range, chemical instability of the compounds particularly in open field conditions and formation of resistant insect strains. Therefore, it has been considered necessary to provide alternative formulations with a view to overcoming such drawbacks and enhancing the positive properties of the insecticides. For example, German Offenlegungsschrift Nos. 2 850 795 and 2 801 916 disclose mixtures of pyrethroids with certain phospho-organic insecticides.

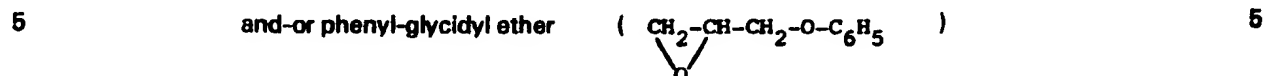
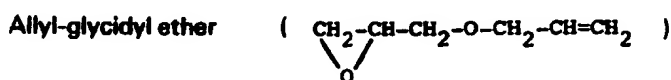
It has now surprisingly been found that certain mixtures of pyrethroids with phospho-organic insecticides possess hitherto unsuspected desirable properties.

Therefore according to the present invention there is provided an insecticide composition comprising:

- (A) from 0.5 to 30% by weight of one or more pyrethroid insecticides selected from:
3-phenoxy-benzyl ester of 2,2-dimethyl-3-(β,β -dichlorovinyl)-cyclopropanecarboxylic acid (common name: permethrin),
 α -cyano-3-phenoxy-benzyl esters of 2,2-dimethyl-3-(β,β -dichlorovinyl)-cyclopropanecarboxylic acid (common name: cypermethrin),
 α -cyano-3-phenoxy-benzyl ester of 2,2-dimethyl-3-(β,β -dibromovinyl)-cyclopropanecarboxylic acid (common name: deltamethrin),
 α -cyano-3-phenoxy-benzyl ester of 2,2-dimethyl-3-(β -fluoro- β -trifluoromethyl-vinyl)-cyclopropanecarboxylic acid,
 α -cyano-3-phenoxy-benzyl ester of 2,2-dimethyl-3-(β -chloro- β -trifluoromethyl-vinyl)-cyclopropane carboxylic acid, and
 α -cyano-3-phenoxy-benzyl ester of 2-(4-chlorophenyl)-3-methyl-butyric acid (common name: phenvalerate);
- (B) from 0.5 to 50% by weight of one or more phosphoorganic insecticides selected from:
O,O-dimethyl-S-methylcarbamoylmethyl-phosphorodithioate (common name: dimethoate),
O,O-diethyl-S-isopropylcarbamoylmethyl-phosphorodithioate (common name: prothoate),
S-alpha-ethoxycarbonyl-benzyl-O,O-dimethylphosphorodithioate (common name: phenthoate) and
diethyl-2,3-dihydro-3-oxo-2-phenyl-6-pyridazinylphosphorothioate (common name: pyridaphenthion);
- (C) from 0.3 to 2.5% by weight of 2-hydroxy-4-octyloxy-benzophenone;
- (D) from 0.5 to 3% by weight of allyl-glycidyl ether and/or phenyl-glycidyl ether;
- (E) from 5 to 25% by weight of a vegetable oil, e.g. selected from one or more of sunflower oil linseed oil rape-seed oil, castor oil, peanut oil and sesame oil;
- (F) 1 to 15% by weight of a surfactant e.g. a surfactant or mixture of anionic and non-ionic surfactants selected from:
calcium dodecylbenzenesulphonate,
triethanolamine dodecylbenzenesulphonate,
polyoxyethylated alkyl phenol containing 8 or 9 carbon atoms in the alkyl moiety and from 5 to 40 moles of ethylene oxide per mole of alkyl phenol,
polyoxyethylated castor oil containing from 10 to 40 moles of ethylene oxide per mole of triglyceride, and
hydrogenated polyoxyethylated castor oil containing from 10 to 40 moles of ethylene oxide per mole of glyceride; and
- (G) in an amount sufficient to attain 100% by weight of composition, an organic solvent or a mixture of organic solvents selected from cyclohexanone and aromatic or alkylaromatic hydrocarbons having from 6 to 12 carbon atoms.

It has been found that the above defined formulations exhibit many unexpected advantages, e.g. the stability of the formulation in the course of time to the high and low temperatures, a very low degradation of the active substances during storage, an improved mutual stability of the active substances in the field and a synergistic insecticide action.

Components (A) and (B) are the active ingredients of the insecticide mixtures according to the invention. The technical grade purity products, commercially available, may be used.
Component (C) is a commercially available UV stabilizer.



which constitute component (D) of the mixture, are known compounds which have chiefly been used as diluents for epoxy resins or as monomers in the preparation of copolymers. These components have not been widely used in pesticide formulations and their use in this field is restricted to a few particular cases.

10 While the use of a vegetable oil in the formulations of the present invention is a critical factor, the particular type of vegetable oil is not critical and the vegetable oils listed as examples of component (E) may be substituted by other vegetable oils having equivalent characteristics. 10

Similarly, while the use of an anionic or non-ionic surfactant is a critical factor, the particular surfactant is not important and those surfactants listed as examples of component (F) may be replaced 15 by other surfactants having analogous properties. 15

The aromatic or alkylaromatic solvents indicated as component (G) do not require a particular purity degree; commercially available mixtures of such hydrocarbons may readily be used.

General examples of compositions according to the invention include the following, in which the component amounts are expressed in percent by weight:

20	(A) pyrethroid	5%	20
	(B) thiophosphoric insecticide	15%	
	(C) benzophenone derivative	0.3%	
	(D) glycidyl ether	2%	
	(E) vegetable oil	10%	
25	(F) surfactant	8%	25
	(G) organic solvent	59.7%	
	(A) pyrethroid	2.5%	
	(B) thiophosphoric insecticide	18%	
	(C) benzophenone derivative	0.5%	
30	(D) glycidyl ether	1%	30
	(E) vegetable oil	15%	
	(F) surfactant	1%	
	(G) organic solvent	62%	
	(A) pyrethroid	7%	
35	(B) thiophosphoric insecticide	49%	35
	(C) benzophenone derivative	1%	
	(D) glycidyl ether	2%	

	(E) vegetable oil	5%	
	(F) surfactant	6%	
	(G) organic solvent	30%	
	(A) pyrethroid	3%	
5	(B) thiophosphoric insecticide	45%	5
	(C) benzophenone derivative	0.5%	
	(D) glycidyl ether	1%	
	(E) vegetable oil	20%	
	(F) surfactant	10%	
10	(G) organic solvent	20.5%	10

The compositions forming the present invention possess many unexpected advantageous characteristics.

As is known, both phosphoric esters and pyrethroids, when conventionally formulated, undergo, in the course of time, a certain degree of degradation which results in a loss of insecticide activity of the formulations. The degradation of such compounds formulated according to this invention is far lower even after long periods of time in comparison to conventional formulations. 15

It is also known that conventional formulations of phosphoric esters may possess low physical stability at both high and low temperatures. The formulations of the present invention are physically stable both at 0°C and at 40 to 50°C and above, even for long periods of time.

The formulations according to this invention generally exhibit little toxicity and little irritation towards the eyes. 20

The combination of pyrethroids and phosphoric esters in the compositions of the invention offers advantages of use since the insecticide activity of the formulation is higher than the combination of the individual components because they exhibit a certain synergistic effect; the active ingredients exhibit a mutual stabilisation in the field after application; the combination of the pyrethroids with the phosphoric esters permits the control of insects which are resistant to one of the two active substances and control of infestation due to acari which generally have little sensitivity to pyrethroids. 25

The advantages offered by the formulations of this invention may be summarised as follows:
chemical stability of the active substances in the formulation,
physical stability of the formulations at high and low temperatures,
low toxicity and low irritant properties of the formulations,
stabilisation of the active substances in the field,
mutual increase in the insecticide activity of the active substances,
insecticide activity against resistant insect strains, and
acaricide activity. 30

No particular techniques are required to prepare the formulations according to the present invention. For example, it is possible to prepare a solution of the various components in the organic solvent, optionally with slight heating, and then finally to add the vegetable oil. 35

For the practical utilisation in agriculture, the formulation of the present invention can be used as such or after dilution in water, depending on the type of application and on the available applicative methods. 40

The amount of composition to be distributed, which varies as a function of different factors, for example the kind and degree of infestation, the culture to be protected, the relative effectiveness of the active substances contained in the compositions also in relation to the preceding factors, the climatic and environmental conditions, generally ranges from 0.5 to 2 Kg/ha. 45

The invention will now be illustrated by the following Examples.

In the Examples some of the surfactants and solvents employed in the compositions are indicated with the following abbreviations:

DBS—TEA—triethanolamine dodecylbenzenesulphonate.

DBS—Ca—calcium dodecylbenzenesulphonate. 50

HOR—25 ETO hydrogenated polyoxyethylated castor oil containing on the average 25 moles of ethylene per mole of substrate. 50

NF—10 ETO polyoxyethylated nonylphenol containing on average 10 moles of ethylene oxide per mole of substrate.

OR—15 ETO polyoxyethylated castor oil containing on average 15 moles of ethylene oxide per mole of substrate.

5 AA—1 mixture of alkyl-aromatic hydrocarbons essentially consisting of compounds having from 8 to 11 carbon atoms. 5

AA—2 mixture of alkyl-aromatic hydrocarbons essentially consisting of compounds having from 9 to 12 carbon atoms.

XIL commercial mixture essentially consisting of xylene isomers.

10

Example 1

10

100 g of a composition (Composition No. 1) according to the invention was prepared consisting of the following ingredients:

	(A) permethrine	5 g	
	(B) dimethoate	15 g	
15	(C) 2-hydroxy-4-octyloxy-benzophenone	0.3 g	15
	(D) phenyl-glycidyl ether	2 g	
	(E) sunflower oil	10 g	
	(F) mixture of DBS—TEA, NF—10 ETO and OR—15 ETO in the ratio 3:5:2	8 g	
20	(G) cyclohexanone	30 g	20
	AA—1	29.7 g	

The composition was prepared by dissolving, under slight heating, component (B) in cyclohexanone and by successively adding components (A), (C), (D), (F) and the alkyl-aromatic solvent (AA—1); the resulting mixture was homogenised and vegetable oil (E) was added thereto.

25 50 g of the abovesaid formulation were divided into several samples and maintained at 0°C for 2 days. No alteration of the composition was observed. 25

A second 50 g portion of the formulation, after having been divided into several samples, was maintained at 40°C for 30 days. After such a period, no alteration of the formulation was observed.

30 The gaschromatographic analysis (GLC) revealed a degradation of dimethoate lower than 2.5% and of permethrine lower than 1%. 30

EXAMPLE 2

Adopting the procedure of Example 1, Composition Nos. 2, 3 and 4 according to the invention were prepared as indicated in the following Table 1.

35 For comparative purposes Composition Nos. 2—A, 3—A, and 4—A were prepared which composition are not known per se, but are of the conventional type, i.e. containing the active substances, suitable solvents and surfactants. These compositions are also reported in the following Table 1. 35

TABLE 1

Compositions according to the invention (Nos. 2, 3 and 4) and comparative composition (Nos. 2-A, 3-A and 4-A).
Each component is expressed in percent by weight.

Components	Composition No.	2	2-A	3	3-A	4	4-A
A	cypermethrine phenvalerate	2.5 —	2.5 —	1.68 —	1.68 —	— 6.9	— 6.9
B	dimethoate prothoate	18.16 —	18.16 —	22 13.5	22 13.5	49 —	49 —
C	benzophenone derivative ⁽¹⁾	0.5	—	0.5	—	1	—
D	phenyl-glycidyl ether	1	—	1	—	2	—
E	sunflower oil	15	—	13	—	5	—
F	DBS-TEA DBS-TEA+NF-10 ETO+OR-15 ETO ⁽²⁾	1 —	1 —	1 —	1 —	— 5	— 5
G	cyclohexanone AA-2 ⁽³⁾	35 to 100	35 to 100	32.5 to 100	32.5 to 100	28 to 100	28 to 100

Notes to Table 1

(1) benzophenone derivative = 2-hydroxy-4-octyloxybenzophenone.

(2) The three surfactants are in the ratio 3:5:2.

(3) to 100 = the balance to 100%.

- 5 A 100 g portion of each of the compositions of Table 1, was divided into various samples, introduced into glass containers and maintained at 54°C for 14 days. 5

At the conclusion of the test, the degradation degree of the active substances was determined by gas chromatography analysis.

- 10 The results, expressed as percent degradation in respect of the initial amount, are recorded in the following Table 2. 10

TABLE 2

Percent degradation of the active substances (Components A and B)
after 14 days at 54°C.

Active substances \ Composition No.		2	2-A	3	3-A	4	4-A
A	cypermethrine	<1	4.8	<1	2.7	—	—
	phenvalerate	—	—	—	—	1.5	9.7
B	dimethoate	1.5	9.9	5.3	10.8	5.1	11.5
	prothoate	—	—	<1	6.4	—	—

EXAMPLE 3

Adopting the procedure of Example 1, the following compositions were prepared:
Composition No. 5

- 15- (A) cypermethrine 3% by weight 15
(B) phenthoate 45% by weight
(C) 2-hydroxy-4-octyloxy-benzophenone 0.5% by weight
(D) phenyl-glycidyl ether 1% by weight
(E) sunflower oil 20% by weight
20 (F) DBS—TEA + NF—10 ETO + OR—15 ETO (3:5:2) 10% by weight 20
(G) AA—2 the balance to 100%.

Composition No. 6

- 25 (A) α -cyano-3-phenoxy-benzyl ester of 2,2-dimethyl-3-(β -fluoro- β -trifluoromethyl-vinyl)-cyclopropane carboxylic acid 3% by weight 25
(B) phenthioate 45% by weight
(C) 2-hydroxy-4-octyloxy-benzophenone 0.5% by weight
30 (D) phenyl-glycidyl ether 1% by weight 30
(E) sunflower oil 20% by weight

(F) DBS—TEA + NF—10 ETO + OR—15 ETO
(3:5:2) 10% by weight

(G) AA—2 the balance to 100%.

Composition Nos. 5 and 6, maintained at 0°C for 2 days, did not exhibit any significant physical alterations. Similarly, Composition Nos. 5 and 6 maintained at 54°C for a 14 day period, did not undergo significant physical alterations, and, furthermore, the GLC analysis, carried out after such a period, revealed that the active substances (Components A and B of both compositions) had not undergone significant degradation.

EXAMPLE 4

10 Determination of the insecticide activity

Using Composition No. 1, a test was carried out to determine the insecticide activity against Cotton Scale (*Pseudococcus edonidum*) on naturally infested *Phylodendron* plants.

As a comparison, the following conventional compositions were prepared and utilised:

Composition 1—A

15 dimethoate 20%

cyclohexanone 25%

DBS—TEA + NF—10 ETO + OR—15 ETO (3:5:2) 10%

xylene the balance to 100%.

Composition 1—B

20 permethrine 25%

OR—10 ETO 10%

xylene the balance to 100%.

The test was accomplished by spraying aqueous emulsions of Compositions 1, 1—A and 1—B onto *Phylodendron* plants which were cultivated in a glass-house and naturally infested with Cotton Scale.

24 days after the treatment, the residual activity was evaluated in comparison with the infestation degree of infested and non-treated plants.

The results obtained after treatment with the compositions in the doses indicated are recorded in Table 3; the data is expressed as percent of residual infestation.

TABLE 3

Insecticide activity (residual activity) in the indicated doses expressed as percent of residual infestation 24 days after the treatment

Composition	Active ingredient dose (g/hl)	Residual infestation (%)
1	15 + 5	0
1—A	20	10.8
1—B	5	8.7

EXAMPLE 5

In the following Table 4, further examples of compositions according to the invention are reported.

The compositions of Table 4, which were prepared according to the general procedure of Example 1, are endowed with the same positive characteristics of the compositions according to the invention illustrated in Examples 1 to 3 that is: physical stability of the formulations at low and high temperature, chemical stability of the active substances and mutual increase in the biological activity of the active ingredients.

5

TABLE 4
Compositions according to the invention.
(Each component is expressed in percent by weight)

Composition No. Component	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
A	Permethrine				30				5						25	
	Cypermethrine	5	7							5	3	5				
	Deltamethrine												8			
	F-CF ₃ (1)			5												
	Cl-CF ₃ (2)					10	5							8		15
B	Phenylacetate					10										
	Dimethoate	15	40		30		30	15			25	15				25
	Prothoate			15								12				
	Phenthoate			15						5			30	30	30	
C	Pyridaphenthion					40			30							
	Benzophenone der. (3)	0.3	1	1	2	1	1	1.5	2.5	1	1	1	1	1	1	2
	Phenyl-glycidyl-ether		2	2			2	1.5	0.5	2	1.5		2	2		1
D	Allyl-glycidyl-ether	2			2	1						2			2.5	

Notes to Table 4

- (1) F—CF₃ = α -cyano-3-phenoxy-benzyl ester of 2,2-dimethyl-3-(β -fluoro- β -trifluoromethylvinyl)-cyclopropanecarboxylic acid.
- (2) Cl—CF₃ = α -cyano-3-phenoxy-benzyl ester of 2,2-dimethyl-3-(β -chloro- β -trifluoromethylvinyl)-cyclopropanecarboxylic acid. 5
- (3) Benzophenone der. = 2-hydrox-4-octyloxy-benzophenone.
- (4) to 100 = the amount required to attain 100% by weight.

CLAIMS:

1. An insecticide composition comprising:
- 10 (A) from 0.5 to 30% by weight of one or more pyrethroid insecticides selected from: 10
3-phenoxy-benzyl ester of 2,2-dimethyl-3-(β , β -dichlorovinyl)-cyclopropanecarboxylic acid,
 α -cyano-3-phenoxy-benzyl esters of 2,2-dimethyl-3-(β , β -dichlorovinyl)-cyclopropanecarboxylic acid,
15 α -cyano-3-phenoxy-benzyl ester of 2,2-dimethyl-3-(β , β -dibromovinyl)-cyclopropanecarboxylic acid, 15
 α -cyano-3-phenoxy-benzyl ester of 2,2-dimethyl-3-(β -fluoro- β -trifluoromethyl-vinyl)-cyclopropanecarboxylic acid,
 α -cyano-3-phenoxybenzyl ester of 2,2-dimethyl-3-(β -chloro- β -trifluoromethyl-vinyl)-cyclopropanecarboxylic acid, and
20 α -cyano-3-phenoxy-benzyl ester of 2-(4-chlorophenyl)-3-methyl-butyric acid 20
(B) from 0.5 to 50% by weight of one or more phospho-organic insecticides selected from:
O,O-dimethyl-S-methylcarbamoylmethyl-phosphorodithioate,
O,O-diethyl-S-isopropylcarbamoylmethyl-phosphorodithioate,
S-alpha-ethoxycarbonyl-benzyl-O,O-dimethylphosphorodithioate, and diethyl-2,3-dihydro-3-oxo-
25 2-phenyl-6-pyridazinylphosphorothioate; 25
(C) from 0.3 to 2.5% by weight of 2-hydroxy-4-octyloxy-benzophenone;
(D) from 0.5 to 3% by weight of allyl-glycidyl ether and/or phenyl-glycidyl ether;
(E) from 5 to 25% by weight of a vegetable oil;
(F) 1 to 15% by weight of a surfactant; and
30 (G) in an amount sufficient to attain 100% by weight of composition organic solvent selected from one 30
or more of cyclohexanone and aromatic or alkylaromatic hydrocarbons having from 6 to 12 carbon atoms.
2. A composition as claimed in Claim 1, in which the vegetable oil is selected from one or more of sunflower oil, linseed oil, rape-seed oil, castor oil, peanut oil, or sesame oil.
- 35 3. A composition as claimed in Claim 1 or Claim 2, in which the surfactant is selected from one or 35
more of calcium dodecylbenzenesulphonate, triethanolamine dodecylbenzenesulphonate, polyoxyethylated alkylphenol containing 8 or 9 carbon atoms in the alkyl moiety and from 5 to 40 moles of ethylene oxide per mole of alkylphenol, polyoxyethylated castor oil containing from 10 to 40 moles of ethylene oxide per mole of triglyceride, and hydrogenated polyoxyethylated castor oil containing from
40 10 to 40 moles of ethylene oxide per mole of triglyceride. 40
4. A composition as claimed in any one of Claims 1 to 3, in which the components A to G are in the following percentages by weight:
- | | | |
|---------------------------------|-------|----|
| (A) pyrethroid | 5% | |
| (B) phospho-organic insecticide | 15% | |
| 45 (C) benzophenone derivative | 0.3% | 45 |
| (D) glycidyl ether | 2% | |
| (E) vegetable oil | 10% | |
| (F) surfactant | 8% | |
| (G) organic solvent | 59.7% | |
- 50 5. A composition as claimed in any one of Claims 1 to 3, in which the components A to G are in 50
the following percentages by weight:

	(A) pyrethroid	2.5%	
	(B) phospho-organic insecticide	18%	
	(C) benzophenone derivative	0.5%	
	(D) glycidyl ether	1%	
5	(E) vegetable oil	15%	5
	(F) surfactant	1%	
	(G) organic solvent	62%	

6. A composition as claimed in any one of Claims 1 to 3, in which the components A to G are in the following percentages by weight:

10	(A) pyrethroid	7%	10
	(B) phospho-organic insecticide	49%	
	(C) benzophenone derivative	1%	
	(D) glycidyl ether	2%	
	(E) vegetable oil	5%	
15	(F) surfactant	6%	15
	(G) organic solvent	30%	

7. A composition as claimed in any one of Claims 1 to 3, in which the components A to G are in the following percentages by weight:

	(A) pyrethroid	3%	
20	(B) phospho-organic insecticide	45%	20
	(C) benzophenone derivative	0.5%	
	(D) glycidyl ether	1%	
	(E) vegetable oil	20%	
	(F) surfactant	10%	
25	(G) organic solvent	20.5%	25

8. A composition as claimed in Claim 1 substantially as herein described with reference to any one of the Examples.

9. A method of controlling infestations due to insects or acari, consisting in distributing in the infested area an effective amount of a composition as claimed in any preceding claim.

30 10. A method as claimed in Claim 9, in which the composition is applied to provide 0.5 to 2 kg/ha of active ingredient (Components (A) and (B)). 30

11. A method as claimed in Claim 9, substantially as herein described with reference to Example 4.